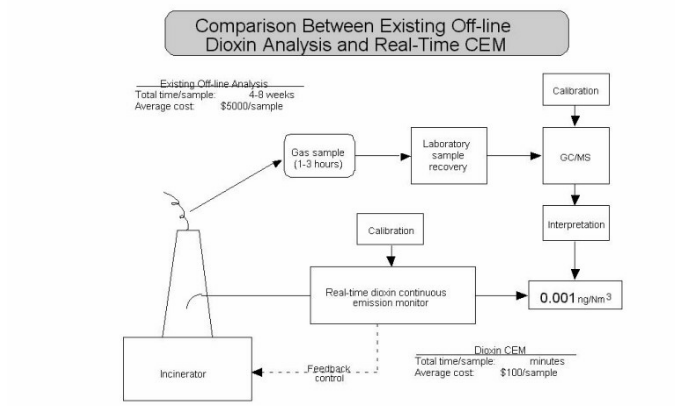
SRI International Corporation

Continuous Emissions Monitor of Dioxins



Technology Need:

Dioxins and furans are generated during the incineration and non-thermal processing of waste materials at DOE remediation sites. The U.S. EPA Office of Solid Waste, which regulates hazardous waste treatment processes, has identified continuous dioxin monitoring as a research priority. However, there are no dioxin Continuous Emission Monitor (CEM) technologies currently available or under development.

Technology Description:

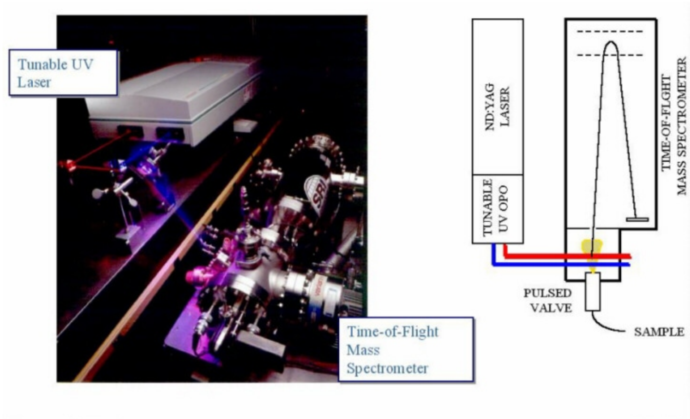
SRI International is developing a real-time, CEM capable of detecting selected dioxin and furan congeners at levels appropriate for studying formation mechanisms and control strategies. Once developed, the proposed instrument will be used to study the emission levels of these key dioxins, leading eventually to an improved understanding of the formation of these molecules and to improved means of monitoring and control.

The approach for an instrument with ultra-trace sensitivity combines optical spectroscopy in the form of resonance enhanced multi-photon ionization (REMPI) enhanced with a pulsed gas jet, and time-of-flight mass spectroscopy (TOFMS). SRI International estimates that a minimum detectability of approximately 0.5 ppt (1 ng/m^3) can be realized for dichlorinated dioxins using the so-called jet-REMPI method.

The phenomenal sensitivity and selectivity afforded by jet-REMPI is directly attributable to the combination of three main components; a pulsed gas-jet, resonance enhanced multi-photon ionization, and a mass spectrometer. All molecules can theoretically exhibit a unique optical absorption signature associated with the specific nature of their electronic, vibrational, and rotational energy levels. However, under normal room temperature conditions much of this uniqueness is lost due overlapping spectroscopic structure, and absorption spectra alone cannot be used to provide chemical discrimination.

In the jet-REMPI instrument, this limitation is overcome by cooling the molecules in a free jet expansion to within a few degrees of absolute zero. As a result, a narrow bandwidth tunable laser source can yield very high selectivity while simultaneously producing positively-charged ions whose molecular weight can be measured by mass spectrometry. In the event that molecular species (other than those of interest) coincidentally absorb the laser radiation and become ionized, they will almost certainly have a different molecular weight, and hence be separable by the mass spectrometer.

This ultra-sensitive chemical detector system uses a pulsed gas valve to introduce sample vapors into the analyzer. Pulsed gas valves provide a number of advantages over continuous gas inlets, including reduced gas flow and hence smaller vacuum pumps, higher local gas densities, well-defined spatial distribution, significantly reduced translational energy distribution orthogonal to the propagation direction, and reduced internal (translational and rotational)



temperatures leading to enhanced spectroscopic resolution. Pulsed valves can operate routinely at temperatures above 250˚ C to accommodate the low volatility of many of the compounds of interest, such as the heavier dioxin congeners and explosives.

REMPI is used as an efficient and highly selective ionization method. In the REMPI process, a molecule is raised from its ground state to its first excited state by one photon, and subsequently ionized by a second photon. Selectivity is provided primarily by the resonance of the first photon with the excited state. Time-of-flight mass spectrometry is the current method of choice for use with REMPI because it is an inherently pulsed technique that matches well with both the pulsed gas inlet, and the pulsed laser ionization. The mass spectrometric requirements are modest, and can readily be achieved with either commercially available devices, or simple, custom components designed to reduce size and weight for a transportable field instrument

Benefits:

▸Real-time CEM will provide immediate feedback on how variations in combustion operating parameters affect dioxin formation and/or destruction

▸More accurate correlations and much more comprehensive data analysis

Status and Accomplishments:

This project was completed in March 2002. During this research effort, SRI made numerous improvements in the jet-REMPI instrument and the project results validate the original concept of using jet-REMPI as the detection method in a dioxin CEM.

SRI has identified a number concepts for instrument improvements that will substantially increase the sensitivity while maintaining the exceptional selectivity required of a dioxin CEM. SRI has also developed several system configurations with varying degrees of functionality that can be further developed and deployed for process monitoring, surrogate measurements, and potentially as a dioxin control CEM. However due to the extremely demanding regulator compliance monitoring requirements involving both congener specificity and sub-part-per-trillion sensitivity with near real time speed, SRI felt it was not yet possible to specify a system configuration for a true dioxin compliance monitor.

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Online Resources:

Office of Science and Technology, Technology Management System (TMS), Tech ID # 2305
http://ost.em.doe.gov/tms

The National Energy Technology Laboratory Internet address is http://www.netl.doe.gov

For additional information, please visit SRI's website:
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